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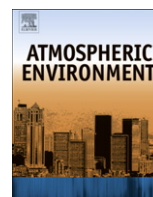
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Surface ozone at the Devils Postpile National Monument receptor site during low and high wildland fire years

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H I G H L I G H T S

- ▶ Diurnal and seasonal O₃ concentrations were measured in remote Sierra Nevada location.
- ▶ Maximum hourly O₃ concentrations were higher in high-fire year than in low-fire year.
- ▶ Local O₃ generation and long range transport contributed to ambient O₃ status.
- ▶ Lowest O₃ was when air masses from above Pacific Ocean crossed California at high altitudes.
- ▶ Highest O₃ was when air masses from near San Francisco Bay crossed California Central Valley.

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Surface ozone (O₃) was measured at the Devils Postpile National Monument (DEPO), eastern Sierra Nevada Mountains, California, during the 2007 (low-fire) and 2008 (high-fire) summer seasons. While mean and median values of O₃ concentrations for the 2007 and 2008 summer seasons were similar, maximum O₃ concentrations in June and August 2008 were higher than in any month of the 2007 summer season. This increase of maximum concentrations in the high-fire year is attributed to emissions of O₃ precursors from wildland fires upwind of DEPO in addition to transport of polluted air from the California Central Valley (CCV) and the San Francisco Bay Area (SFBA). Analysis of backward trajectories for high O₃ episodes in June 2007 and 2008 showed the lowest O₃ pollution at DEPO when air masses originated over the Pacific Ocean (PO) and passed from West to East over PO and CCV at high altitudes. The highest O₃ levels occurred when air masses originated in the vicinity of SFBA, swept through CCV in the NW–SE direction before reaching DEPO at low altitudes. Diurnal O₃ concentrations were characterized by a sharp increase early morning and maximum values in late afternoon, followed by gradual evening decreases with very low pre-dawn minima, a phenomenon explained by local generation of O₃ combined with the long range transport of polluted air masses from CCV, boundary layer destruction and surface deposition. Once in 2007, and 3 times in 2008, the 8-h average concentration exceeded 75 ppb, counting towards exceedance of the present primary Federal O₃ standard (4th highest 8 h concentration <75 ppb over 3 years). The California 8-h average standard (<70 ppb) was exceeded 5 times in 2007 and 6 times in 2008, and these instances counted towards exceedance of the newly proposed primary Federal standard (4th highest 8-h concentration <70 ppb over 3 years). In addition, in 2008, the California 1-h average standard (<90 ppb) was exceeded 3 times. The proposed Federal secondary O₃ standard of 13 ppm h was exceeded reaching 16 ppm h in 2007 and 15 ppm h in 2008 that indicates potentially phytotoxic effects on local flora.

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1. Introduction

Information about air quality in remote areas of the United States, especially in high elevation mountain locations, including the Sierra Nevada Mountains (SNM) in California, is still limited due to difficult access, lack of electrical power, and potential damage to monitoring equipment from adverse weather conditions and/or vandalism (Bytnerowicz et al., 2000). Passive samplers operating on a principle of diffusion of gases into collecting media have greatly helped to fill this knowledge gap for various gaseous pollutants (Krupa and Legge, 2000). Consequently, passive samplers have been used to investigate the distribution of ozone (O_3) in the entire SNM (Frączek et al., 2003), and in smaller areas such as Sequoia & Kings Canyon NP (Ray, 2001; Bytnerowicz et al., 2002), Yosemite NP (Ray, 2001) or the San Joaquin River (SJR) drainage in SNM (Cisneros et al., 2010). However, since passive samplers do not provide real-time concentrations of pollutants, their usefulness for understanding O_3 toxicity – which strongly depends on short-term peak concentrations – is limited. In this regard, low-cost, real-time portable UV absorption monitors have been useful (Bognar and Birks, 1996) and have been successfully used for evaluation of real-time O_3 concentrations in various remote western US areas including Yosemite NP (Burley and Ray, 2007) and the White Mountains in California (Burley and Bytnerowicz, 2011). The *in situ* real-time O_3 measurements in mountain locations are of high importance because predictions with existing models can be highly inaccurate due to complex topography, inconsistent dispersion patterns, varying meteorological conditions, and changing O_3 formation rates (Barna and Lamb, 2000; Millan et al., 2000).

Western portions of Sequoia & Kings Canyon NP and Yosemite NP of the SNM are considered some of the most polluted US rural areas (CASTNET, 2011) due to their proximity to the highly-polluted California Central Valley (CCV) and the San Francisco Bay Area (SFBA). Summer-time measurements in densely forested Sequoia & Kings Canyon NP showed a pronounced decline (1.6 ppb km^{-1}) of O_3 concentrations with increasing distance from the pollution source area and elevation in more remote central and eastern Park locations (Bytnerowicz et al., 2002). However, in Yosemite NP and along the SJR trans-Sierra transect, in a landscape more open than in Sequoia & Kings Canyon NP, a decline of O_3 concentrations from its highly polluted western part to cleaner eastern areas was less pronounced (0.7 ppb km^{-1} , and 0.2 ppb km^{-1} , respectively) (Burley and Ray, 2007; Cisneros et al., 2010).

Emissions from wildland fires can have pronounced effects on ambient O_3 concentrations in remote areas (Jaffe and Wigder, 2012) including those in the western United States (Jaffe and Ray, 2007; Pfister et al., 2008). These effects could be expected in areas downwind of the northern California Fire Siege that occurred in summer 2008. During that event, the area of burned forest was the highest since fires were recorded in California – about 1.24 million acres (500,000 ha). Most of the fires started on June 20–21, 2008 when >2000 of them were ignited by about 6000 lightning strikes in remote areas of northern and central California. About 90% of those fires were burning in northern portion of the state, and many of them lasted through most of the summer season (http://www.fire.ca.gov/index_incidents_overview.php).

Good air quality in national parks, national monuments and other Class I wilderness areas is a major concern for federal, state and local air resources managers (Peterson et al., 1992). Impaired air quality and elevated concentrations of atmospheric pollutants, especially those regulated at the national and state levels, may have negative effects on human health and ecological resources. From this perspective, O_3 is especially important because it is a criteria pollutant with well-known deleterious effects on humans and

vegetation (Manning, 2005). The present Federal O_3 primary (health) and secondary (welfare effects, including ecological) standard states that the 3-year average of the 4th highest daily maximum 8-h average concentrations must not exceed 0.075 ppm (<http://www.epa.gov/air/criteria.html>). It has been proposed that the O_3 primary standard should be lowered to 0.070 ppm, with the secondary standard set as the W126 parameter with a value of 13 ppm h as the 3 month, 12 h (daytime) cumulative dose (http://www.epa.gov/air/ozonepollution/pdfs/201107_OMBdraft-OzoneRIA.pdf). In California, the O_3 standard is set as an 8-h average not to exceed 0.070 ppm and a 1-h average not to exceed 0.090 ppm (<http://www.arb.ca.gov/newsrel/nr042805.htm>).

Information on air quality at the Devils Postpile National Monument (DEPO) is important for NPS managers because it receives a high number of visitors (health issues) and contains valuable & fragile ecosystems that are potentially susceptible to various stressors, including air pollution. Objectives of this study were: (1) evaluate O_3 air pollution at DEPO, and, (2) improve knowledge regarding potential effects of wildland fires on air pollution at remote, high elevation SNM areas. The study was performed during the low-fire (2007) and high-fire (2008) summer seasons.

2. Methodology

2.1. Location

DEPO is located near the NE end of the SJR drainage close to the SNM crest (Fig. 1). An air pollution monitoring site was situated at the Soda Springs Meadow (latitude = 37.6293°N , longitude = -119.0848°W , elevation = 2306 m) adjacent to the middle SJR fork. The site was approximately 100 m SW of the DEPO Visitors Center.

2.2. Meteorological data

Temperature and relative humidity (RH) data for 2007 and 2008 summer seasons were acquired from the meteorological station located near the air pollution monitoring equipment (see above). That station did not provide reliable wind data and therefore such data were obtained for the 2007 and 2008 from the Hurley weather station (latitude = 37.0153°N , longitude = -119.5678°W). The Hurley station is located near the outlet of the SJR drainage into the San Joaquin Valley (SJV). Until 2004, the Hurley site and the old DEPO meteorological station (latitude = 37.6300°N , longitude = -119.0933°W) showed very similar wind patterns, which suggests that wind data from the Hurley site are representative for the SJR drainage.

2.3. Air pollution monitoring

Ozone concentrations were measured with a 2B Technologies Model 202 Ozone Monitor (Bognar and Birks, 1996), which was powered by a 12-V battery connected to a 90-W solar panel. The sampling inlet consisting of a downward-facing 47 mm diameter Teflon filter holder with a $2 \mu\text{m}$ Teflon filter membrane was positioned $\sim 1.5 \text{ m}$ above ground level and was connected directly to the monitor by a 2 m long Teflon tubing of 6.35 mm outside diameter. The monitor was enclosed within a weatherproof plastic case and the sampling inlet was covered by a plastic rain shield. Ozone concentrations were measured continuously at 10-s intervals, and were recorded into internal monitor memory as 5-min averages. These 5-min averages were later downloaded from the monitor to a laptop computer and converted into hourly averages. Pre- and post-deployment calibrations were performed in the



Fig. 1. Location of the Devils Postpile National Monument (DEPO) in the Sierra Nevada Mountains. SEKI – Sequoia & Kings Canyon National Park; Yose – Yosemite National Park.

beginning and end of each monitoring period to verify accurate monitor performance; these calibrations yielded results consistent with previous investigations (Burley and Ray, 2007). The hourly values reported here have an estimated precision of ± 5 ppb and an estimated accuracy of $\pm 6\%$.

2.4. Fire smoke contours

Smoke distribution contours were based on smoke images obtained from the GOES satellite (<http://www.oso.noaa.gov/goes/>). These images provided three different smoke densities: $5 \mu\text{g m}^{-3}$ for light, $16 \mu\text{g m}^{-3}$ for medium, and $27 \mu\text{g m}^{-3}$ for thick, in the column of air assigned to each polygon. The smoke densities were

obtained by converting aerosol optical depth values from the GOES Aerosol and Smoke Product (GASP) (<http://www.ssd.noaa.gov/PS/FIRE/GASP/gasp.html>) into aerosol concentrations. In this work only values $>16 \mu\text{g m}^{-3}$ were used and were overlaid on backward trajectories for selected days during the June 2008 high O_3 event.

2.5. Backward trajectories with fire information

The regional-scale transport patterns responsible for bringing air masses to DEPO during the high- O_3 days were investigated by conducting backward trajectory calculations with the online version of the HYSPLIT model (Draxler and Hess, 1997, 1998; Draxler, 1999; Draxler and Rolph, 2010; Rolph, 2010). Calculations

were performed using the 40 km EDAS (Eta Data Assimilation System) archived meteorological data for 5 days in 2007 (June 14, 15, 16, 18, and 19) and 4 days in 2008 (June 24, 25, 26, and 27), when O₃ ambient standards were exceeded. For comparison, backward trajectories for low O₃ days during those events (June 17, 2007 and June 23 and 28, 2008) were also included. All backward trajectories ended at 10:00 PST at DEPO (e.g., at the beginning of stable phase of photochemical O₃ generation after its active phase has been completed) with a run time of 48 h and arrival heights of 10, 300 and 500 m above model ground level (AGL).

2.6. Statistical analysis

A regression model was fitted to estimate the shape and significance of the relationships between O₃ and the weather data to further understand the diurnal O₃ patterns:

$$O_3 \approx \text{intercept} + s_1(\text{temp}) + s_2(\text{rh}) + s_3(\text{windd}, \text{by} = \text{ihr}) + \text{error} \quad (1)$$

where: s_1, s_2, s_3 , are smooth spline functions (Hastie and Tibshirani, 1990; Wood, 2006) and the error term is autoregressive random noise. The smooth functions were used in the regression in order to accommodate possible non-linear relationships between O₃ and the weather variables. In particular, it was anticipated that the relationship with wind direction would be nonlinear and periodic with values at 0° and 360° being the same. We estimated two separate curves for the wind direction variable (windd). The first was for the effect of wind during the middle of the day (between 1400 and 1800 PST) and second during remaining 20 h of the day. This is similar to adding an interaction term between the variables windd and ihr (where ihr is an indicator variable for mid-day or not midday). An autoregressive error term was used to take into account the serial correlations in the hourly data (R Development Core Team, 2011).

2.7. Ozone exposure indices

Ozone exposure indices (SUM00, SUM60, SUM70, SUM80, and W126) were calculated for 24 h for four months (June–September) using the Ozone Calculator program (William Jackson, USDA Forest Service, <http://webcam.srs.fs.fed>). The SUM00 index is the sum of all hourly concentrations without a threshold. SUM60, SUM70, and SUM80 are the sums of all hourly concentrations above 60 ppb, 70 ppb, and 80 ppb, respectively. The W126 is a sigmoidally weighted index (Lefohn and Runeckless, 1987) where higher concentrations have a greater weight. The SUM60 and W126 indices have been suggested as the most acceptable and most commonly used vegetation exposure indices in the U.S. (U.S. EPA, 1996; Musselman et al., 2006). A new secondary standard proposed by the U.S. Environmental Protection Agency, W126 for 12 h between 08:00–20:00 PST for 3 months (July 1–September 30) (http://www.epa.gov/air/ozonepollution/pdfs/201107_OMBdraft-OzoneRIA.pdf) was also calculated.

3. Results

3.1. Ozone seasonal trends

In general, the O₃ concentrations at DEPO in 2007 and 2008 were similar (Table 1, Fig. 2). While median values for individual months in 2007 remained stable, in 2008 the September values were lower. As the year progressed, maximum values decreased from ~86 ppb in June 2007 and ~100 ppb in June 2008 to ~80 ppb and ~75 ppb in September 2007 and 2008, respectively.

Table 1

Comparison of 2007 and 2008 basic statistics for O₃ concentrations at DEPO for the June 3–September 29 periods (ppb).

	2007	2008
Min.	0.0	0.0
1st Qu.	18.3	15.4
Median	38.4	33.8
Mean	37.0	34.7
3rd Qu.	53.9	52.1
Max.	86.2	100.0

Maximum values were higher in 2008 than in 2007 (100.0 and 86.2 ppb, respectively), however, the 2008 overall median and means (33.8 and 34.7 ppb, respectively) were similar to those in 2007 (38.4 and 37.0 ppb, respectively).

3.2. Ozone diurnal trends

Diurnal patterns of O₃ and meteorological variables that affect O₃ chemistry had similar characteristics in 2007 and 2008 and therefore these two summer seasons of data were combined. Ozone concentrations were low at night, rapidly increased between 07:00 and 09:00 PST, remained roughly constant until about 14:00 PST, increased to maximal values at about 17:00 PST, and then steadily declined to the minimal values at 04:00–05:00 PST. The sharp increase of morning O₃ values corresponded with a rapid increase in temperature, a decrease of RH, and change of wind direction from NE (~20°) to S and SSW (~200°). The wind direction shifted again at ~14:00 PST to WSW (~240°) and finally around 22:00 PST it shifted back to NE (~20°) (Fig. 3).

Ozone concentrations were strongly correlated with temperature and RH, with the highest O₃ occurring at ~23 °C and ~25% RH (Fig. 4a and b). The estimated significant increase in O₃ values was seen when mid-day winds were coming from WSW (highest values seen around 250°) (Fig. 4c). The relationship with wind direction was not significant for the non-mid-day hours (Fig. 4d).

The standard deviation of O₃ values was 18.6 ppb. The corresponding value for the residuals after removing the effects of temperature and RH was 10.2 ppb, and 9.8 ppb when wind direction was added to the model. The R² value (variance explained) for the model with all three weather variables was 0.72. Additionally, wind direction seemed to account for most of the O₃ increase around ~17 PST (Fig. 5) when the wind was predominantly from W and SW (between 180 and 270°) as seen in Fig. 3.

3.3. High O₃ events and exceedances of air pollution standards

In summer 2007, the highest O₃ concentrations at DEPO were recorded during the 6-day period of June 14–19, with hourly O₃ reaching a maximum value of 86 ppb on June 15 (Fig. 6a). The 8-h averages for this period exceeded the California air quality standard of 70 ppb during five out of six consecutive days (June 14–16 and 18–19) and 75 ppb 8-h average that counts towards an exceedance of the Federal air quality standard on June 19. Hourly O₃ concentrations in excess of 80 ppb were later observed on July 7 and 27, August 23 and 26, and September 12, but none of these episodes was associated with a violation of the California or Federal 8-h O₃ standards. In summer 2008, elevated O₃ levels were measured during the June 24–27 period, with maximum 1-h concentration of 100 ppb on June 25 (Fig. 6b). The 8-h averages for this period exceeded 70 ppb on all four days and 75 ppb on June 25 and 26. In July, hourly O₃ concentration exceeded 80 ppb during five days (July 11, 12, 19, 24, and 26) and the 70 and 75 ppb 8-h averages were exceeded on July 11. In August, O₃ levels were >80 ppb on August 14–15, and the 70 ppb 8-h average was exceeded on August 14.

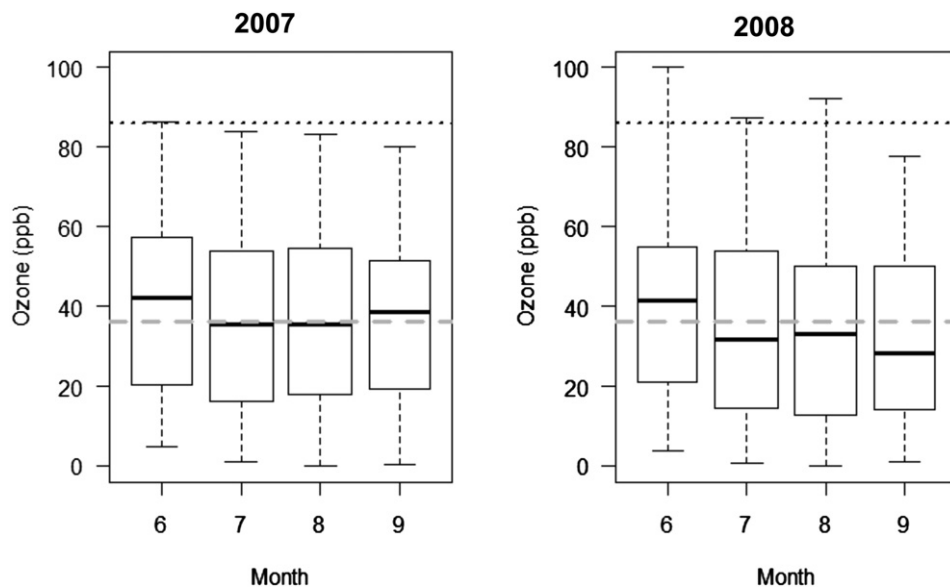


Fig. 2. Boxplots showing the median, middle 50% and range of hourly O_3 concentrations at DEPO for each month for 2007 and 2008 (6 – June; 7 – July; 8 – August; and 9 – September). Horizontal gray line at 36.4 ppb is the overall medial level for both years.

During 1 day in 2007 and 3 days in 2008, the 8-h averages of 75 ppb were exceeded and those instances counted towards exceedance of the current Federal primary standard. However, that standard would have not been violated since it is defined as the 3-year average of the 4th highest maximum 8-h average concentrations in a given year. Potentially, however, the newly proposed Federal standard defined as the 8-h average of 70 ppb could be violated because during 5 days in 2007 and 6 days in 2008 that concentration was exceeded. Exceedances of the 8-h average concentration of 70 ppb mean, however, that the California standard calculated for a single season was violated in both years. In addition, the California 1-h standard of 90 ppb was exceeded 3 times in 2008 (Table 2).

3.4. Backward trajectories for high O_3 events

Trajectories for the analyzed days of the high- O_3 events differed depending on the specified arrival height (10, 300, and 500 m AGL). Although the backward trajectories for the 2007 event (low-fire year) varied among individual days, in general the air masses originating over PO, SFBA or CCV were funneled into the SJR drainage before reaching DEPO. That was the case for the high- O_3 days of June 14, 15, 16, 18, and 19 (Fig. 7a, b, c, e and f). For the low- O_3 day (June 17), the air masses that originated over PO crossed CCV in the W–E direction, with those of the 10 and 500 m AGL moving over CCV high above the ground (Fig. 7d). In 2008 (high-fire year),

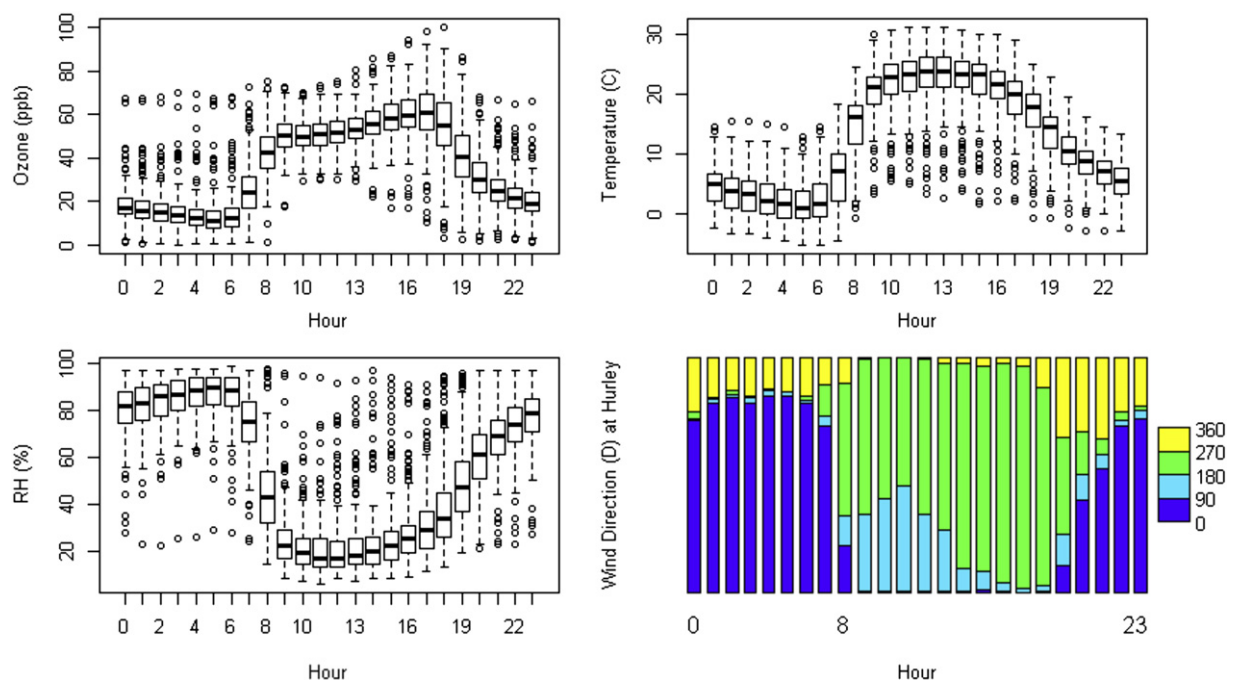


Fig. 3. Boxplots showing diurnal patterns of O_3 hourly concentrations, temperature and relative humidity at DEPO and wind direction at Hurley.

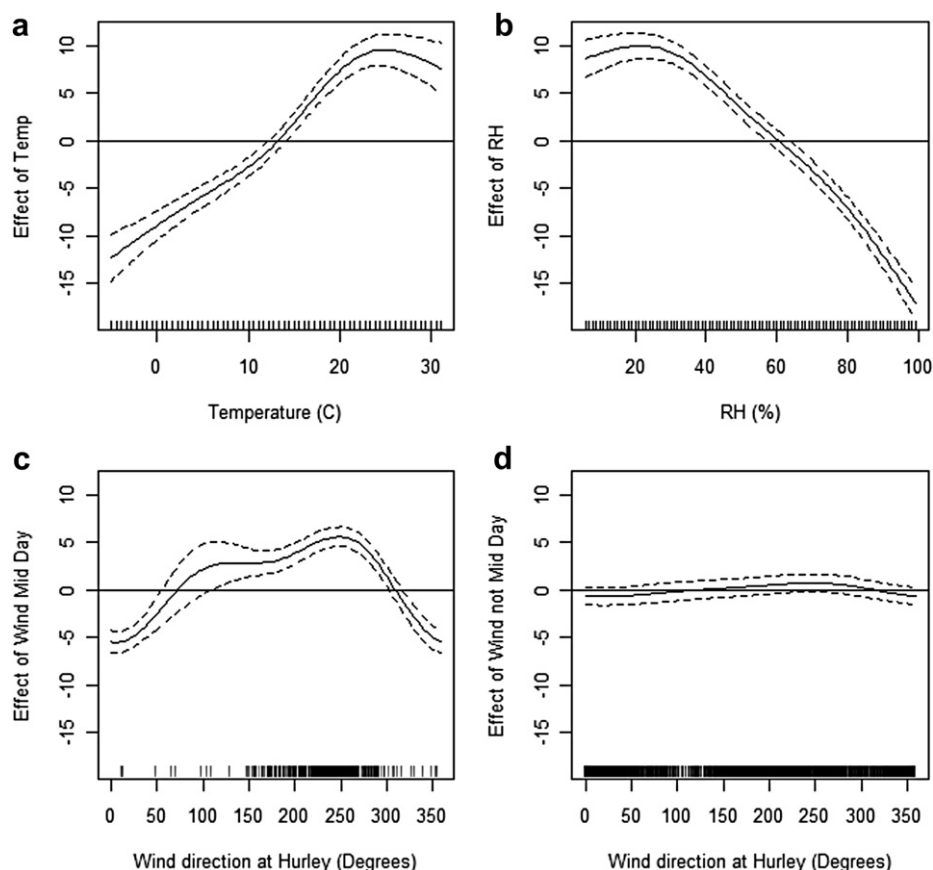


Fig. 4. Estimated partial effects of the weather variables: (a) temperature; (b) relative humidity; (c) wind in mid-day, 14:00–18:00 PST; (d) wind in rest of day (19:00–14:00 PST). These graphs represent the spline functions s_1, s_2, s_3 in Equation (1) to show the increase or decrease of O_3 values relative to an overall mean (represented by the horizontal line at zero). The dashed lines are approximate point-wise 95% confidence bounds. A variable has no significant effect if the zero horizontal line is entirely within the 95% confidence bounds. Hatch marks at the bottom of each panel are the location of the observed values.

smoke from multiple fires initiated by lightning strikes on June 20 and June 21 spread quickly and by June 22 covered large portions of northern and central California. On June 24 the smoke extended into Oregon and Nevada, and on June 25 it also covered most of California and expanded into PO. A gradual decrease in the area

covered by smoke was observed on June 26 and continued through June 27 and 28. On June 23 (low- O_3 day), similarly as for the low- O_3 day of June 17, 2007, the air masses originated over PO and moved at high elevations over CCV into DEPO (Fig. 8a). In 2008, during all high- O_3 days, the air masses were crossing SFBA, CCV and SNM

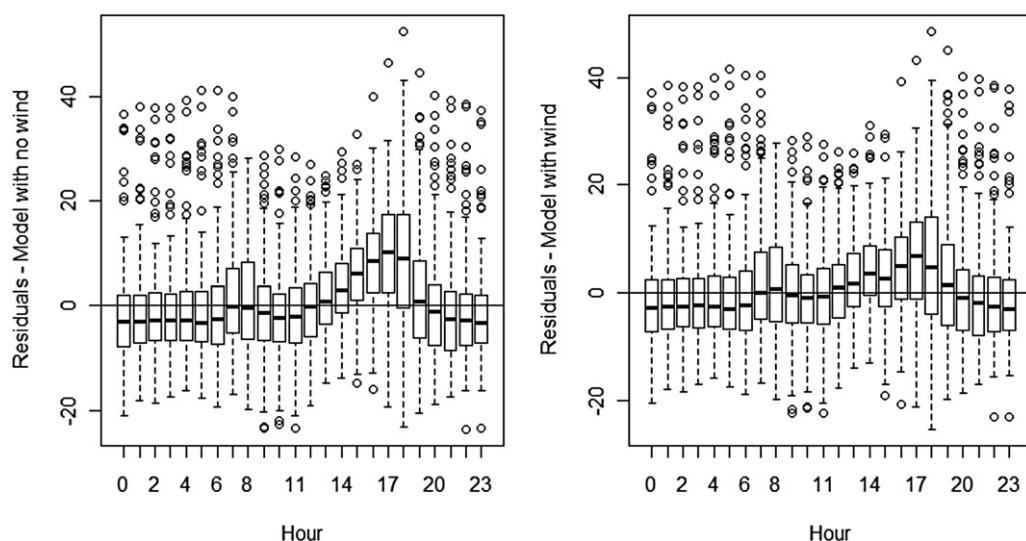


Fig. 5. Boxplots of residuals after removing estimated effects of temperature and relative humidity (left panel) and temperature, relative humidity and wind direction (right panel). Note that almost all the diurnal patterns seen in the ozone levels in Fig. 3 are ‘explained’ by the weather variables in the model. The wind direction seems to have accounted for most of the O_3 increase around 17:00 PST.

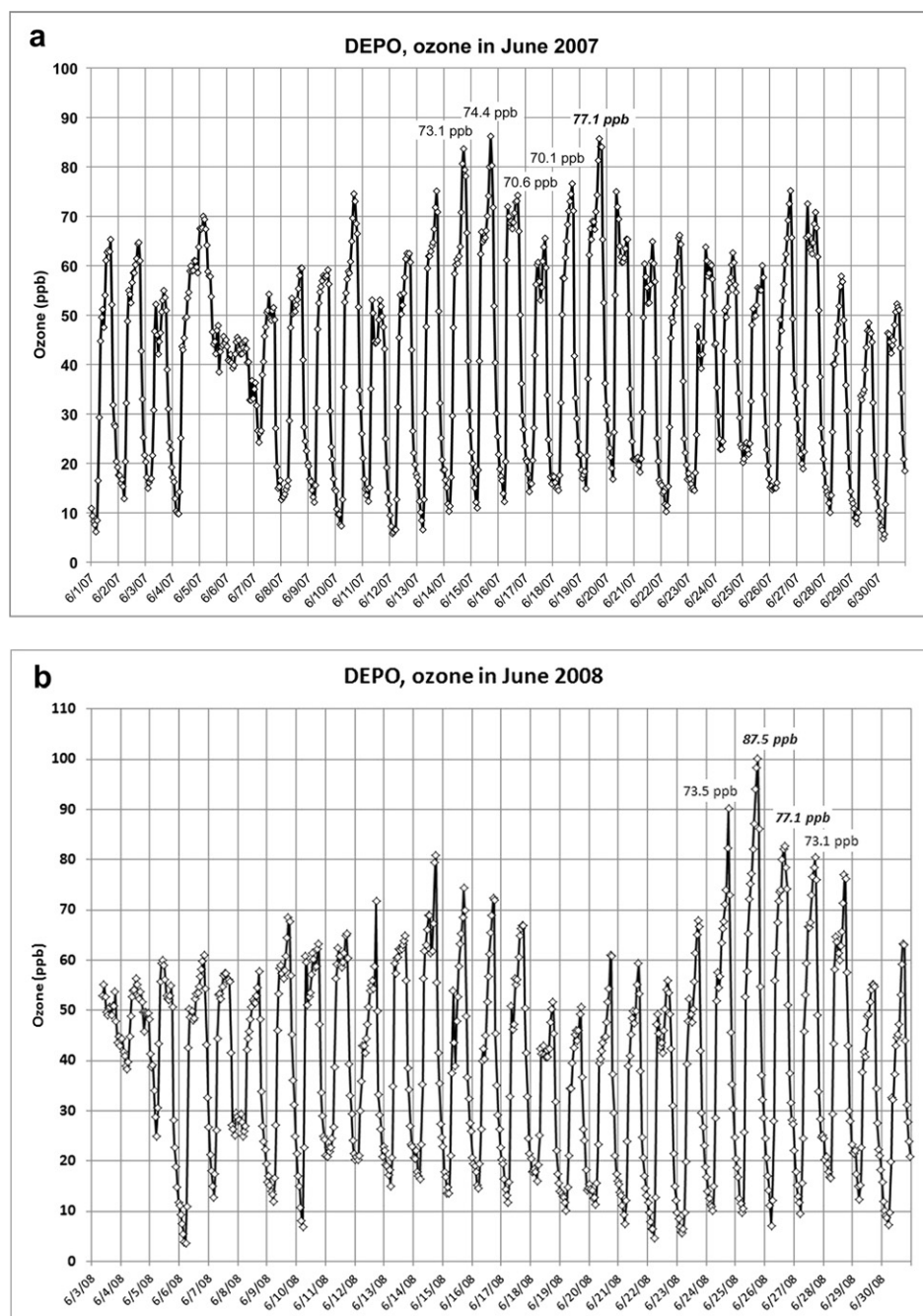


Fig. 6. Time series plot of O_3 concentrations at DEPO during high O_3 events: (a) June 2007 and (b) June 2008. The 8 h maximum averages that exceed the California standard of 70 ppb are shown in regular font; those that count towards exceedance of the US Federal standard of 75 ppb are presented in the bold italic font.

Table 2
Exceedances of primary federal and California standards for O_3 at DEPO.

Standard	2007	2008
US federal present standard, 75 ppb (8 h)	1 ^a	3 ^a
US federal, proposed 70 ppb (8 h)	5 ^b	6 ^b
California 70 ppb (8 h)	5 ^c	6 ^c
California 90 ppb (1 h)	0 ^d	3 ^d

^a Contribution to the exceedance of the standard.

^b Enough occurrences >70 ppb to count towards an exceedance of the proposed standard.

^c Standard exceeded in both years.

^d Standard exceeded only in 2008.

covered with smoke before reaching DEPO (Fig. 8b–e). On the second low- O_3 day of that event (June 28), the air masses from northern SNM reached DEPO from N (Fig. 8f). In general, the June 2008 backward trajectory patterns were more variable than those in June 2007.

3.5. Ozone exposure indices

All calculated O_3 exposure indices used for evaluation of potential phytotoxic effects were similar in 2007 and 2008 (Table 3). The W126 daytime values calculated for the July 1–

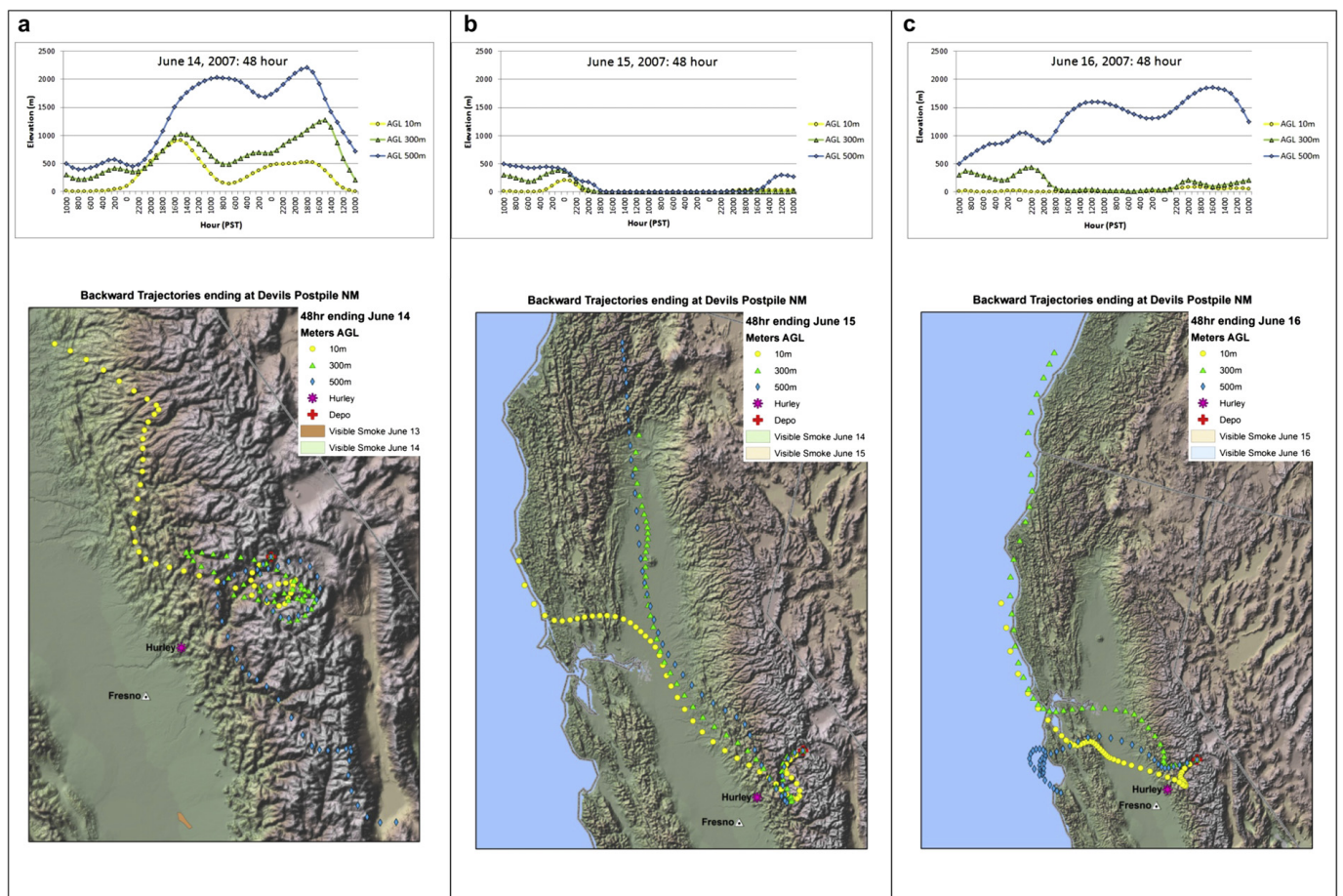


Fig. 7. Backward trajectories for the DEPO site during the high- O_3 event of June 2007: (a) June 14; (b) June 15; (c) June 16; (d) June 17; (e) June 18; (f) June 19.

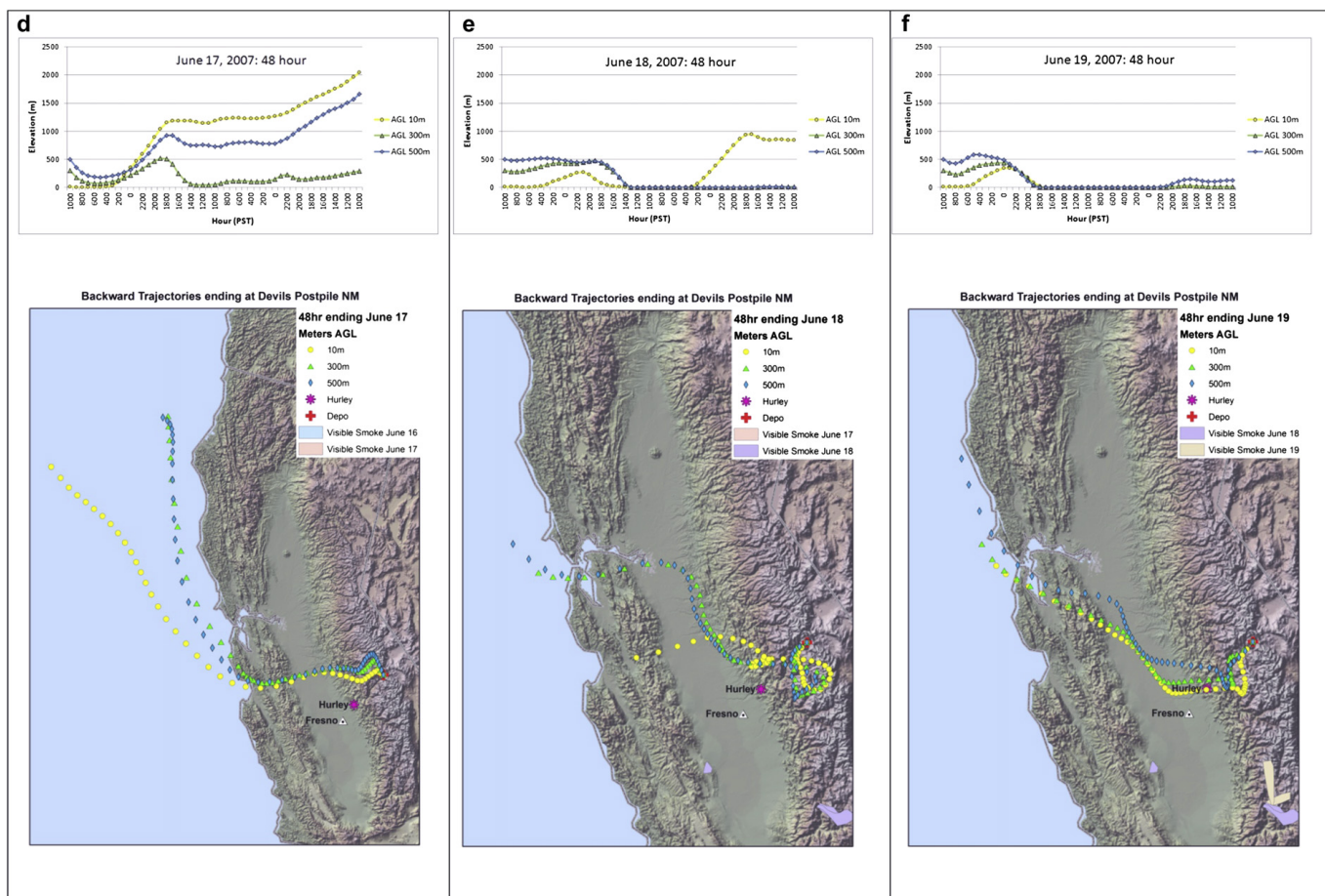


Fig. 7. (continued).

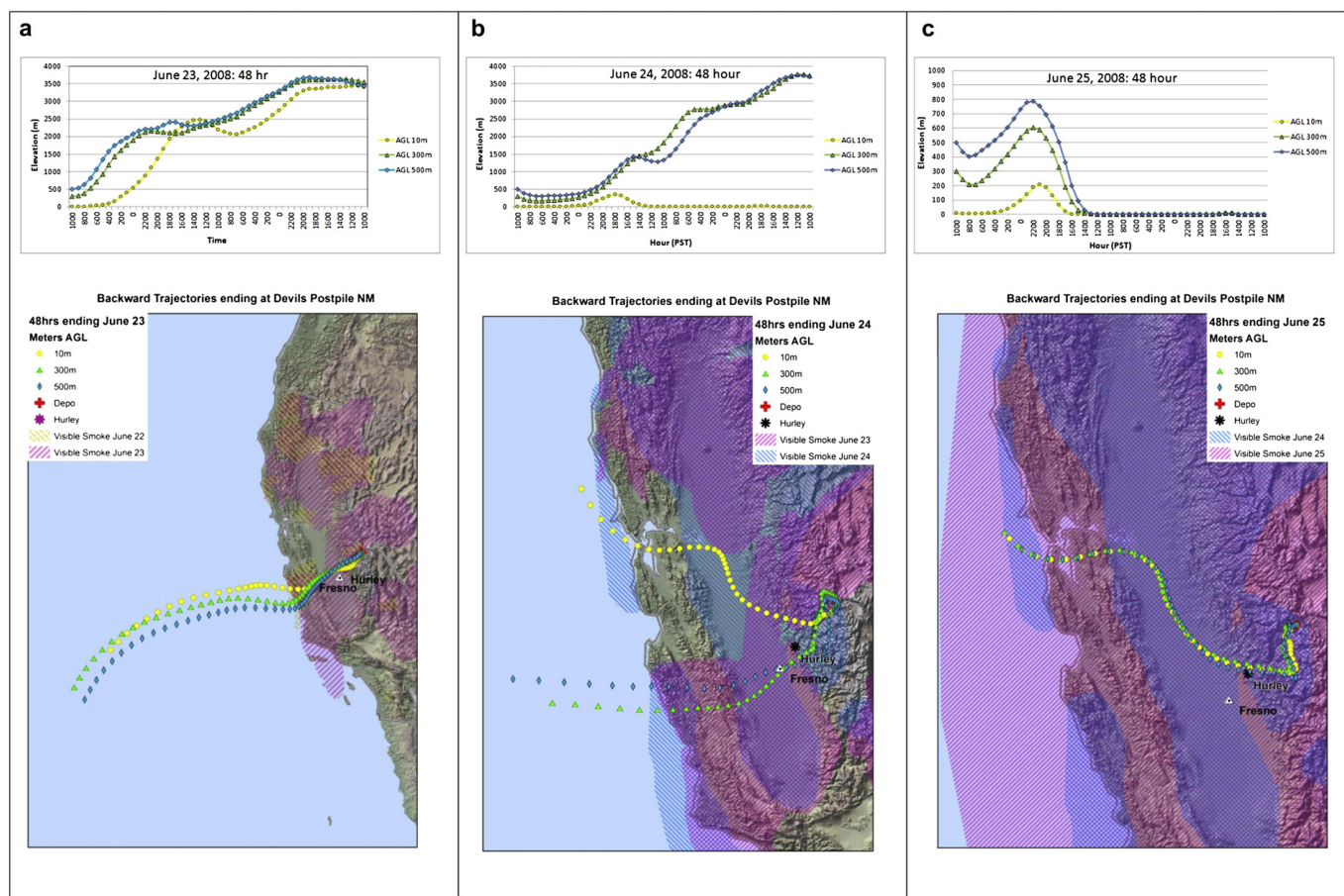


Fig. 8. Backward trajectories for the DEPO site during the high-O₃ event of June 2008: (a) June 23; (b) June 24; (c) June 25; (d) June 26; (e) June 27; (f) June 28.

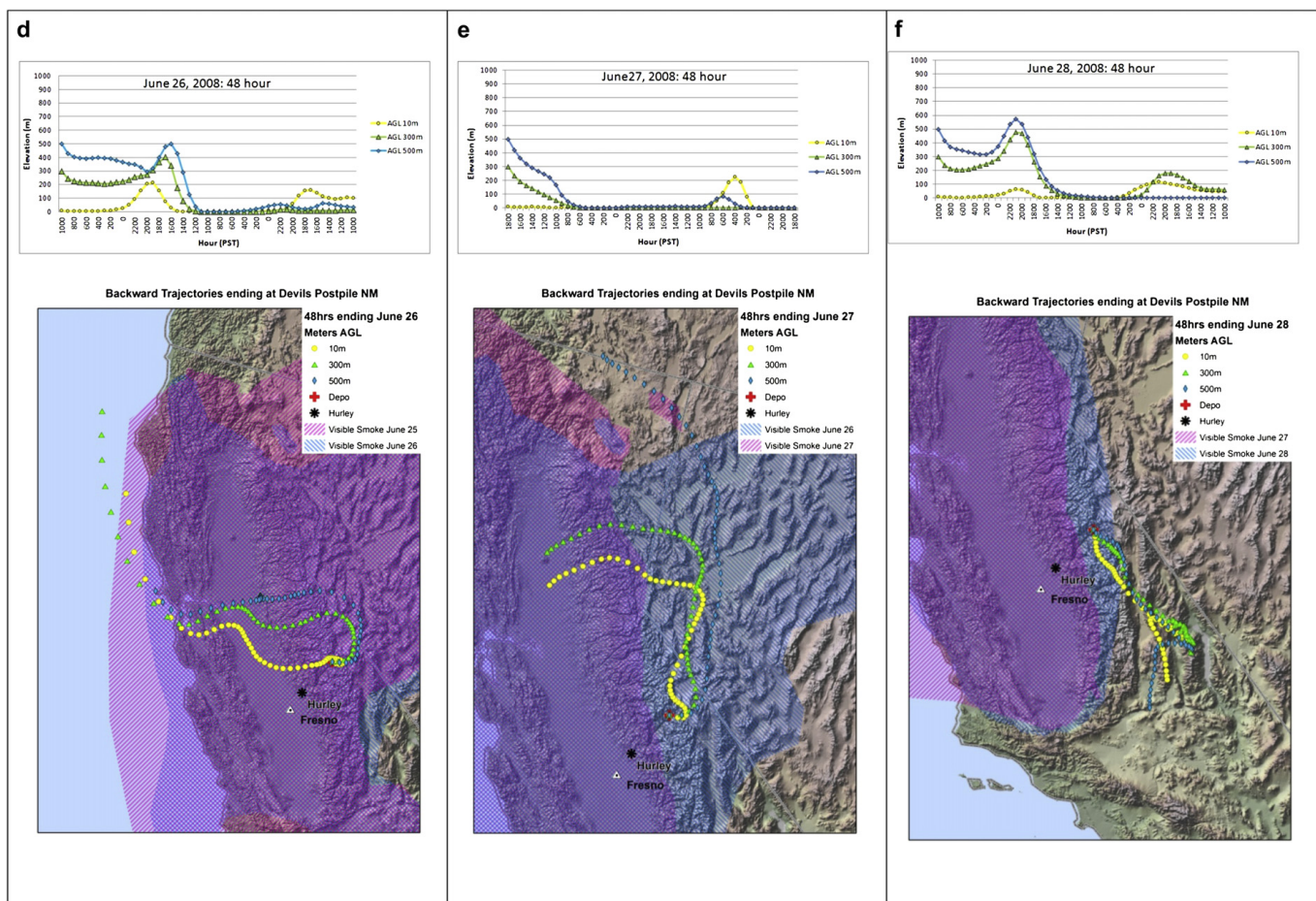


Fig. 8. (continued).

Table 3
Exposure indices for evaluation of O₃ potential phytotoxicity at DEPO.

Ozone exposure index (ppm h)	2007	2008
SUM00	110	98
SUM60	29	23.5
SUM70	8	8
SUM80	1	3
W126 – 24 h	21	19
W126 – 12 h, 8:00–20:00 PST (proposed Federal secondary standard)	16	15

September 30 periods were 16 ppm h in 2007 and 15 ppm h in 2008. These values were above the newly proposed secondary O₃ standard of 13 ppm h indicating potential phytotoxic effects on sensitive flora at DEPO.

4. Discussion

Generally, DEPO can be considered as a low pollution site when compared with other locations in central SNM (Cisneros et al., 2010). However, due to the strongly pronounced diurnal differences, with low O₃ values at night and high daytime concentrations reaching >80 ppb in 2007 and even ~100 ppb in 2008, DEPO did end up with several days exceeding the California O₃ air pollution standards in both years.

Ranges of diurnal concentrations and their temporal patterns at DEPO were similar to those at the Tuolumne Meadows and Mirror Lake sites of Yosemite NP (Burley and Ray, 2007), and also at Shaver Lake on the W end of the SJR drainage, although the mean daily concentration at that site was ~15 ppb higher (Van Ooy and Carroll, 1995). The O₃ values at DEPO increased rapidly between 07:00 and 09:00 PST, concurrently with rising temperatures and decreasing RH. The initial early morning rapid O₃ increase was most likely caused by the break-up of the stable inversion layer formed the night before. Ozone-rich air from above (i.e., from the free troposphere above the boundary layer) was mixed downwards and O₃ concentrations rose rapidly. At this point, efficient local photochemical production of O₃ could also commence given the high daytime radiation and temperature typical for this part of the Sierra, with the observed rate of O₃ generation depending on concentrations of available O₃ precursors. Judging from low NO₂ concentrations determined with passive samplers and slightly elevated NO concentrations (likely from local emissions), photochemical O₃ generation was probably NO_x limited (Hakola et al., 2003). By mid-morning the atmosphere approached a well-mixed state that kept the O₃ levels stable for a few hours followed by a slight increase in the afternoon. It is interesting to note that this late morning – early afternoon O₃ plateau (~50 ppb) was similar to the background values measured at a number of remote, high elevation sites in the White Mountains ~70 km E of DEPO (Burley and Bytnerowicz, 2011). The afternoon O₃ levels continued to increase until they reached a maximum at ~17:00 PST. Local emissions of volatile organic compounds (VOCs) and NO from the Diesel-powered shuttle buses used for transportation of the DEPO visitors (as well as emissions from other vehicles), stagnant air, as well as high temperatures and solar radiation all contributed to local O₃ production during afternoon hours. An additional supply of O₃ precursors and O₃ from the long-range upslope transport of steadily moving polluted air masses from CCV along the SJR drainage in the SW–NE direction could also enhance the late-afternoon O₃ formation. This general movement of air masses was typical for the middle part of SNM (Carle, 2006). Compared to the CCV locations such as Fresno, where maximum O₃ values were at about 14:00–15:00 PST, the O₃ maximum at DEPO occurred later. After about 17:00 PST a rapid drop-off of solar irradiance occurred

causing a temperature decrease and RH increase that shut off the mixing from aloft and local photochemical production. A temperature inversion started to form and increased O₃ deposition to the lush alpine meadow vegetation started taking place. Ozone concentrations continued dropping throughout the night, down to <20 ppb just before sunrise. This scenario is similar to that described for high elevation meadows in Yosemite NP (Burley and Ray, 2007).

During most days of the June 2007 high-O₃ event, backward trajectories showed air masses corresponding to three different arrival heights (10, 300 and 500 m AGL) coming from SW and S up the SJR drainage. Prior to these hours, the backward trajectories typically approached from W or NW either after sweeping through the low elevation W slopes of SNM or through CCV. In most cases, these trajectories originated either in central CCV or over PO near SFBA. During the 2008 high-O₃ event, movement of air masses into DEPO was less predictable and more variable than during the 2007 event. In all cases these trajectories were passing through areas covered with smoke from the wildland fires, resulting in higher maximum O₃ concentrations than during the 2007 low-fire event. However, the O₃ increases caused by wildland fire smoke were much lower than those recorded at a receptor site close to the October 2007 large wildland fires near San Diego (Bytnerowicz et al., 2010). During the low-O₃ days, air masses originated over PO and moved at high elevations over CCV into DEPO. This scenario confirms findings from the White Mountains where the lowest O₃ was observed during days when air masses originated over PO (Burley and Bytnerowicz, 2011). It should be stated that while the source–receptor relationships of atmospheric composition can be investigated using the backward trajectory techniques (Fleming et al., 2012), the HYSPLIT backward trajectory calculations provide a good representation of large-scale flows but are less suitable for local or mesoscale variations (<http://vista.cira.colostate.edu/docs/WRAP/Modeling/>). The overall error estimate for a HYSPLIT trajectory calculation is approximately 15–30% of the total travel distance. In addition, the HYSPLIT model does not include boundary layer effects and does not consider independent thermodynamic effects (http://www.arl.noaa.gov/HYSPLIT_FAQ.php).

The 2008 wildland fires affected air quality in large areas of California, Oregon and Nevada as the smoke distribution shows. These effects were seen as the increased Aerosol Optical Thickness (AOT) in southern British Columbia as well as elevated O₃ and carbon monoxide (CO) at Mount Bachelor in central Oregon and Whistler Mountain in southern British Columbia (McKendry et al., 2011). It has been well established that emissions from wildland fires contain VOCs, CO and NO_x (Yokelson et al., 2007; Goldammer et al., 2009) that contribute to O₃ formation. While increased O₃ concentrations have been reported over large areas of western United States downwind of wildland fires (Jaffe et al., 2008; Pfister et al., 2008), detailed analysis for remote sensitive receptor sites, such as DEPO, is still very limited.

Ozone data from DEPO show multiple exceedances of both the California standard (8-h average of 70 ppb) and 8-h average of 75 ppb which count toward potential violation of the Federal O₃ primary standard. These exceedances correspond to ambient O₃ levels that occasionally may be unhealthy to both DEPO visitors and NPS staff. Calculated O₃ exposure indices for vegetation were much lower than those calculated for the highly polluted San Bernardino Mountains of southern California (Bytnerowicz et al., 2008). The W126 values based on 24 h measurements (21 and 19 ppm h in 2007 and 2008, respectively) were also much lower than the 2002 value of 43 ppm h calculated for the nearby Starkweather Lake site (Cisneros et al., 2010). The 12 h based W126 values of 16 and 15 ppm h for 2007 and 2008, respectively, were just above the proposed Federal secondary standard of 13 ppm h. Our data

indicate that the DEPO O₃ levels could be potentially phytotoxic to local flora, including highly sensitive species such as ponderosa or Jeffrey pines (Bytnerowicz and Grulke, 1992).

5. Conclusions

1. Elevated O₃ at DEPO resulted mostly from local photochemical cycles, with an additional contribution from long-range transport of polluted air masses from SFBA and CCV.
2. Emissions from the 2008 northern California forest fires increased maximal (hourly) O₃ concentrations.
3. Low O₃ concentrations were observed when air masses originating over PO crossed CCV at high elevation before reaching DEPO.
4. High O₃ concentrations were observed when air masses swept through the SFBA and CCV at low elevations before reaching DEPO.
5. Occasionally O₃ concentrations exceeded the California air quality standards and contributed to potential exceedances of the Federal primary standard. This indicates a risk to sensitive individuals and a need for long-term O₃ monitoring.
6. Although O₃ concentrations at DEPO were generally lower than in other SNM areas, there was a potential for modest phytotoxic effects on sensitive plants. Therefore direct observations of potential impacts on plants are recommended.

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